KINETIC MODELING OF HARDWOOD PREHYDROLYSIS. PART I. XYLAN REMOVAL BY WATER PREHYDROLYSIS[1]

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ABSTRACT

The kinetics of xylan removal from quaking aspen, paper birch, American elm, and red maple by water prehydrolysis (autohydrolysis) was reevaluated, and additional data for the water prehydrolysis of southern red oak were obtained. Xylan removal from these hardwood species can be modeled kinetically as the sum of two parallel first-order reactions—one fast and one slow. The rate constant for the fast reaction is highly correlated with the rate constant for the slow reaction for all species studied. The rate constant for initial xylan removal usually reported in the literature is actually a complex function of the rate constants for both the fast and slow reactions and is based solely on the initial data points. This paper presents an improved method for modeling xylan removal that allows modeling throughout the course of its reactions. The reason there are two different rates of xylan removal can be more easily explained on the basis of accessibility rather than any variability in the polymeric structure of the xylan being removed. Thus, the slow rate may be due to a portion of the xylan being embedded within or attached to the lignin via lignin-carbohydrate bonds.

Keywords: Xylan, prehydrolysis, water prehydrolysis, autohydrolysis, kinetics, hardwoods, aspen, *Populus tremuloides,* birch, *Betula papyrifera,* elm, *Ulmus americana,* maple, *Acer rubrum,* southern red oak, *Quercus falcata.*

INTRODUCTION

Renewed interest in the utilization of wood and wood residues as sources of energy and chemical intermediates has necessitated an understanding of the kinetics of wood fractionation. This understanding is required in order to model the overall reactions that occur and to allow the design and evaluation of processes used to separate wood into its basic chemical constituents (i.e., cellulose, hemicellulose, and lignin).

Reanalysis of published data (Springer and Zoch 1968) on the water prehydrolysis of quaking aspen (*Populus tremuloides* Michx.), paper birch (*Betula papyrifera* Marsh.), American elm (*Ulmus americana* L.), and red maple (*Acer rubrum* L.) and the analysis of recently acquired data for the water prehydrolysis of southern red oak (*Quercus falcata* Michx.) are presented here.

The hemicelluloses in wood (predominately *O*-acetyl-(4-*O*-methylglucurono)xylan in hardwoods) are more readily hydrolyzed than is cellulose. Therefore, many recent schemes that have been proposed for the utilization of wood as a

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source of chemicals and liquid fuels include a prehydrolysis step to remove the hemicellulosic sugars as a water-soluble prehydrolysate. The lignocellulosic residue is then saccharified to give glucose and a lignin residue.

Prehydrolysis, which can be effected by acids such as dilute mineral acid or the acetic acid released on hydrolysis of hemicellulose acetate by water (autohydrolysis), is by no means a new process. Based largely on the pioneering work of Richter (1956), prehydrolysis is presently used prior to the production of kraft dissolving pulps, especially those produced from hardwoods. The Masonite process (Mason 1921) uses prehydrolysis prior to the production of fiberboard and hardboard products. Water prehydrolysis is the fundamental basis of the more recent Iotech explosion process (Marchessault and St.-Pierre 1978; Marchessault et al. 1979) and the Stake process (Bender 1979), both of which are being exploited commercially to utilize wood for energy, chemicals, and animal feed. Thus, knowledge about the kinetics of prehydrolysis has a broad range of applicability to present wood utilization processes and is of fundamental interest to the development of new processes.

Previous research showed that based on a plot of the log of xylan remaining versus time, the removal of xylan hemicellulose from wood appears to occur with an initial fast phase followed by a slower second phase (Simmonds et al. 1955; Kobayashi and Sakai 1956; Springer et al. 1963; Springer and Zoch 1968). Springer et al. (1963) and Springer and Zoch (1968) obtained estimates of the pseudo-first order rate constants for the initial fast removal of xylan from various hardwoods. These estimates were obtained from the initial slope of a semilog plot of xylan remaining versus time. The individual rate constants for the fast and slow phases were not determined, nor were the experimental data modeled to demonstrate their fit to any kinetic system.

In connection with research on the prehydrolysis of hardwoods, it was of interest to determine the apparent kinetic rate constants for both the fast and slow reaction phases for prehydrolysis of hardwoods, and to determine that portion of xylan more resistant to prehydrolysis.

RESULTS AND DISCUSSION

The kinetic model that best fits the removal of xylan from wood during water prehydrolysis is the combination of two parallel pseudo-first order reactions (one fast and one slow). The following reactions can be postulated to explain the overall apparent kinetics of xylan removal:

$$\left.\begin{array}{l} X_f \xrightarrow{k_f} \\ \\ X_s \xrightarrow{k_s} \end{array}\right| \rightarrow \text{soluble oligosaccharides} \qquad (1)$$

where

X_f = amount of more reactive xylan remaining after any reaction time (t),
k_f = apparent pseudo-first order rate constant for the fast reaction,
X_s = amount of more resistant xylan remaining after any reaction time,
k_s = apparent pseudo-first order rate constant for the slow reaction.

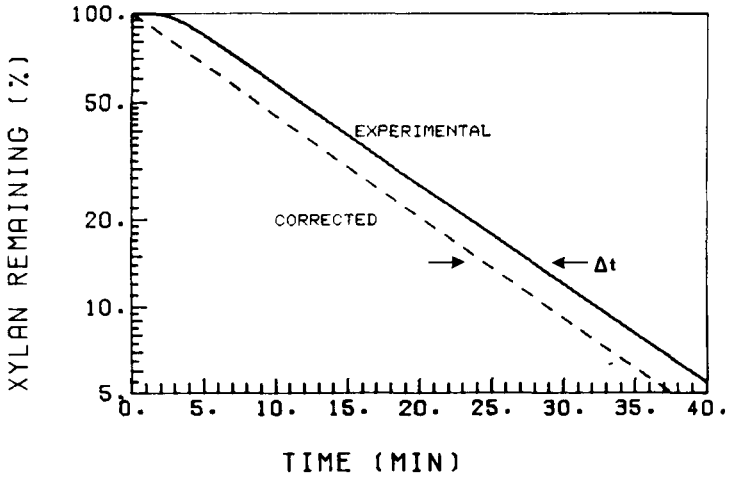

FIG. 1. Graphical representation of the time correction, Δt, for correcting experimental data to iso-conditions.

For these pseudo-first order reactions

$$X_f = X_f^0 e^{-k_f t} \tag{2}$$

and

$$X_s = X_s^0 e^{-k_s t} \tag{3}$$

where X_f^0 and X_s^0 are the initial amounts of X_f and X_s, respectively. Thus, because the total amount of xylan, X_t, remaining after any reaction time is

$$X_t = X_f + X_s \tag{4}$$

then

$$X_t = X_f^0 e^{-k_f t} + X_s^0 e^{-k_s t} \tag{5}$$

Further, because

$$X_f^0 + X_s^0 = X_t^0 \tag{6}$$

where X_t^0 = total amount of xylan at $t = 0$, then

$$X_t = (X_t^0 - X_s^0) e^{-k_f t} + X_s^0 e^{-k_s t} \tag{7}$$

Derivation of Eq. 7 assumes both isothermal and isoacidic conditions. However, experimental considerations dictate that the first few minutes of the reaction will be neither isothermal or isoacidic. As the system reaches isothermal conditions, and as liberation of acid from the wood (predominately acetic acid) approaches completion, the rate of removal of xylan becomes parallel to that at isothermal, isoacidic conditions (Fig. 1). Correction of the data to isothermal, isoacidic conditions can be made empirically by subtracting the factor Δt from the reaction time as indicated in Fig. 1. The magnitude of the correction is a function of the

TABLE 1. *Reaction rate constants for xylan removal from various hardwoods.*

Species	Reaction conditions	Calculated[a]					Reported[b]	Uronic anhydride[c]
		k_1	k_2	X_2^0/X_1^0	Δt	k_i	k_i	
		min^{-1}		%	*min*	*min*$^{-1}$		%
Southern red oak	H_2O/171.1 C	0.0807 ± 0.0061	0.0049 ± 0.0008	26.1 ± 2.5	2.6 ± 0.3	0.0609	—	4.2
Paper birch	H_2O/170 C	0.0628 ± 0.0085	0.0036 ± 0.0009	28.4 ± 4.7	4.5 ± 0.6	0.0460	0.0387	4.5
Red maple	H_2O/170 C	0.0485 ± 0.0037	0.0024 ± 0.0007	19.7 ± 3.0	3.5 ± 0.5	0.0394	0.0350	4.5
Quaking aspen	H_2O/170 C	0.0317 ± 0.0032	0.0018 ± 0.0008	24.0 ± 4.4	4.0 ± 0.8	0.0245	0.0242	4.7
American elm	H_2O/170 C	0.0193 ± 0.0023	0.0009 ± 0.0014	15.7 ± 6.5	0.0 ± 1.3	0.0164	0.0124	5.4

[a] From nonlinear least squares fit of data to Eq. 8. Data are reported ± asymptotic standard error.
[b] Springer and Zoch (1968).
[c] Analyzed by Browning method (1949) on extractives-free wood.

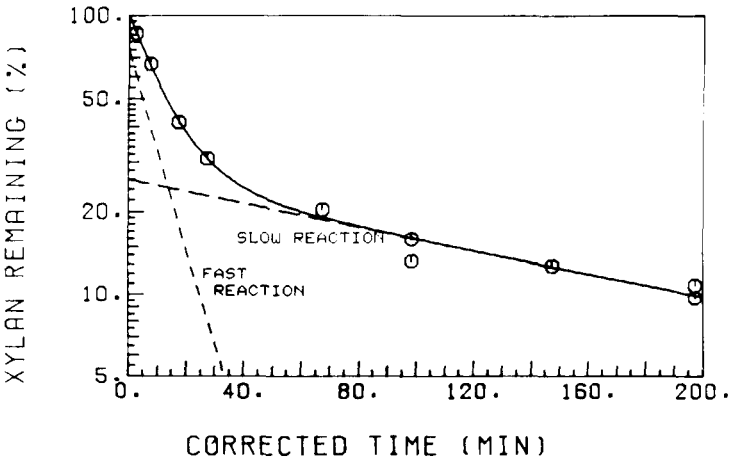

FIG. 2. Semilog plot of xylan remaining versus time (corrected) for water prehydrolysis of southern red oak at 171.1 C. The circles are experimental data. The solid line is the curve for a nonlinear least squares fit of the data to Eq. 8. The progress of the fast and slow reactions is indicated by the broken lines.

heat transfer characteristics of the reaction system and the energy of activation for the reaction. Thus, the equation for total xylan remaining becomes

$$\frac{X_t}{X_t^0} = \left(1 - \frac{X_s^0}{X_t^0}\right)e^{-k_f(t-\Delta t)} + \frac{X_s^0}{X_t^0}e^{-k_s(t-\Delta t)} \tag{8}$$

Equation 8 was fitted by a nonlinear least squares method to the data reported by Springer and Zoch (1968) and to the data for the prehydrolysis of southern red oak using the Statistical Analysis System (SAS) nonlinear procedure (version 79.3A) (Helwig and Council 1979). The results of this analysis are presented in Table 1. Figures 2 and 3 show that in all cases the values predicted from Eq. 8 are in agreement with the experimental data.

Differentiation of Eq. 7 shows that the initial rate of xylan removal at t = 0 is

$$\left(\frac{dX_t}{dt}\right)_{t=0} = -k_f(X_t^0 - X_s^0) - k_sX_s^0 \tag{9}$$

Thus, the pseudo-first order rate constant for the initial fast removal of xylan (k_i) determined by Springer and Zoch (1968) can be related to k_f, k_s, and X_s^0/X_t^0 by the following

$$k_i = k_f\left(1 - \frac{X_s^0}{X_t^0}\right) + \frac{k_sX_s^0}{X_t^0} \tag{10}$$

Table 1 gives a comparison of k_i calculated from k_f, k_s, and X_s^0/S_t^0 and the estimate of k_i obtained by Springer and Zoch from the initial slope of a semilog plot of xylan remaining versus time. The two values differ in some cases by up to 23%. This can be attributed in part to the assumption by Springer and Zoch that the initial portions of the semilog plots of xylan removal are linear, and in part to experimental errors associated with the data.

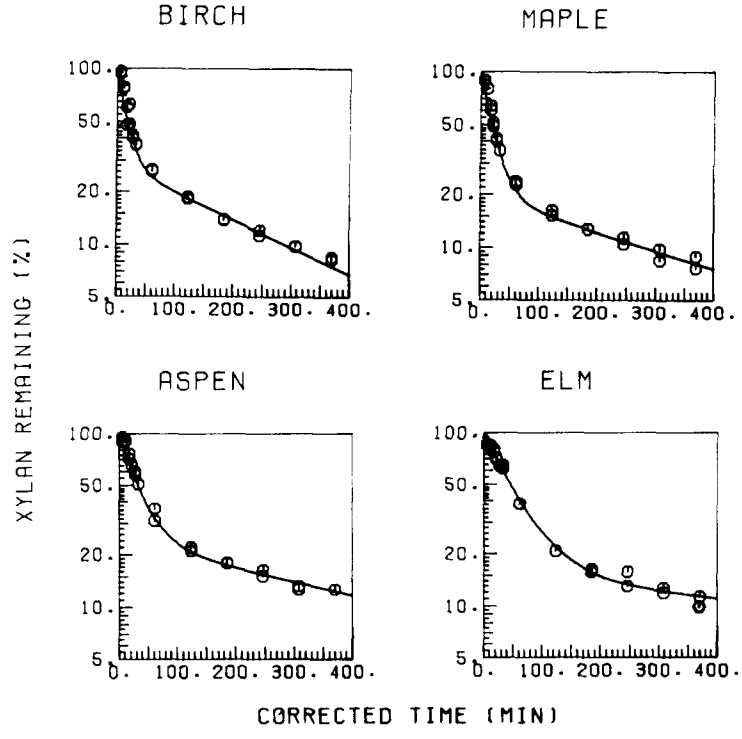

FIG. 3. Semilog plot of xylan remaining versus time (corrected) for water prehydrolysis of paper birch, red maple, quaking aspen, and American elm at 170 C. The circles are experimental data (Springer and Zoch 1968). The solid line is the curve for a nonlinear least squares fit of the data to Eq. 8.

Springer and Zoch also pointed out that there seems to be an inverse relationship between the uronic acid content and the initial fast xylan removal. Indeed, it is well known that the β-1,4-glycosidic bonds in *O*-acetyl-(4-*O*-methylglucurono)xylan corresponding to the β-1,4-glycosidic bond in aldotriouronic acid (Fig. 4) are substantially less reactive than the other β-1,4-glycosidic bonds within the xylan polymer (Harris 1975). Thus, as the uronic acid content of the xylan increases, the number of the more easily cleaved bonds decreases. As a consequence, the rate of xylan removal declines. The prehydrolysis of southern red oak also appears to follow this trend (Table 1). This trend is more clearly seen if one plots the ratio uronic acid/xylan versus k_f (Fig. 5). The deviations about this trend are due to variations in the acid concentration within the reaction condition arising from variations in the acetyl and ash contents of the wood. In addition the reaction temperature for the southern red oak is higher than that for the other wood samples, which also leads to a deviation. The rate constant for the southern red oak in Fig. 5 was calculated using the Arrhenius equation and assuming an activation energy of about 118 kJ/mole for the hydrolysis of xylan (Springer 1966).

The uronic acid content of the southern red oak was determined by a spectrophotometric procedure (Scott 1979) and by the Browning method (1949). The uronic acid contents of the other species were also determined by the Browning

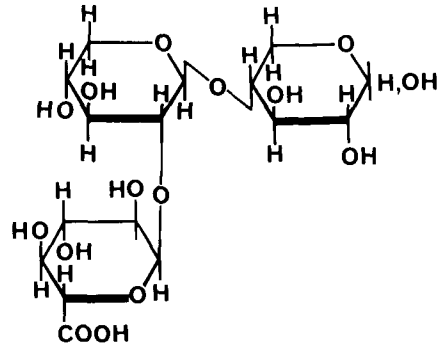

FIG. 4. Aldotriouronic acid.

method. From literature data (Scott 1979; Whistler et al. 1940), it appears that the Browning method gives a higher value than the spectroscopic method due to release of CO_2 from components other than uronic acid in the wood. For purposes of comparison between species, only the Browning values have been used. This, however, is another source of possible deviation from the line in Fig. 5.

It is interesting to note that while k_f and k_s vary from species to species, they are highly correlated (correlation coefficient = 0.993) for all species (Fig. 6). The reason there are two different rates of xylan removal can be more easily explained on the basis of accessibility than by any variability in the polymeric structure of the xylan being removed. Thus, a portion of the xylan could be intimately associated with the lignin matrix by being embedded within that matrix or linked to the lignin by lignin-carbohydrate bonds (Adler 1977). Evidently more than one bond type may be involved (Minor 1982; Obst 1982). A portion of these bonds appears to be lignin-xylan ester linkages via the uronic acid side chain (Obst 1982;

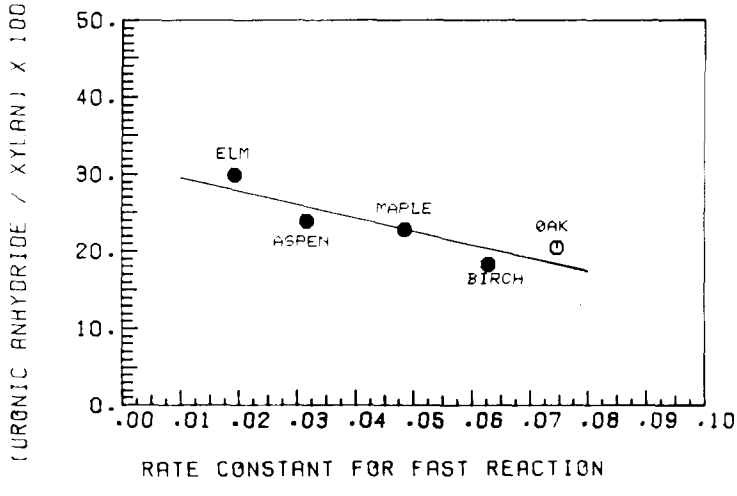

FIG. 5. Plot of (uronic anhydride content/xylan content) × 100 versus k_f. The solid symbols are taken from Table 1. The open symbol is the calculated rate constant for southern red oak at 170 C.

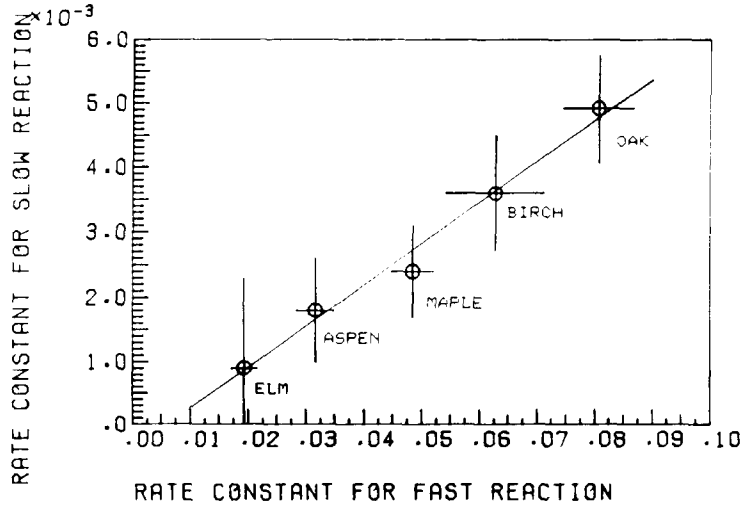

FIG. 6. Relationship between k_f (the rate constant for the fast reaction) and k_s (the rate constant for the slow reaction).

Das et al. 1981). Further work is needed to fully evaluate these and other possibilities.

EXPERIMENTAL

Air-dried whole wood chips of southern red oak (*Quercus falcata* Michx.) were ground in a Wiley mill to pass a 4-millimeter screen. The fraction having a 20- to 30-mesh size was used for all experiments. The summative analysis of this material is presented as Table 2.

Prehydrolysis

All reactions were conducted in a reaction bomb made from a 152-millimeter section of 316 stainless steel tubing (~9.8-mm outside diameter by 0.8-mm wall) sealed at one end by welding a small section of a stainless steel rod into place. The open end was sealed with a stainless steel Swagelock cap. The cap had a small hole drilled through the top. A silicon rubber septum was placed between the reaction vessel and the cap.

About 600 milligrams of wood meal of known moisture content were accurately weighed and placed in the tared reaction bomb. A vacuum was drawn on the sealed bomb using a hypodermic needle passed through the septum and connected to an aspirator. Sufficient water was introduced into the evacuated bomb with a syringe to give a liquid to solid ratio of 3:1. The reaction vessel was then hand centrifuged to ensure the movement of the water throughout the sawdust bed. This was facilitated by the vacuum previously drawn on the system.

The reaction vessel was heated in a constant temperature oil bath (171.1 ± 0.1 C) for the desired length of time. On removal, the reaction vessel was submerged in cold water to stop the reaction. The time from submersion in the oil bath to submersion in the cold water bath was recorded as the reaction time.

Before opening the bomb, any pressure was relieved with a hypodermic needle.

TABLE 2. *Summative analysis of southern red oak wood.*

Component	Percent[a]
Glucan	38.9 ± 0.8
Xylan	19.1 ± 1.2
Mannan	2.1 ± 0.3
Araban	0.9 ± 0.2
Galactan	1.7 ± 0.3
Lignin	21.5 ± 1.4
Extractives[b]	6.7 ± 0.1
Uronic anhydride[c]	3.0 ± 0.2 (4.2)
Acetyl	3.5
Ash	0.3
Other	2.3

[a] Based on oven-dried wood weight.
[b] Extracted with benzene/alcohol.
[c] Determined as in Scott (1979), except that the value in parentheses was determined as in Browning (1949).

The contents were washed from the bomb with hot water onto a tared sintered glass funnel. The residue was washed with approximately 100 milliliters of boiling water and dried in a vacuum oven at 60 C overnight. The filtrate was collected and diluted to a known volume.

Sugar analyses

Sugar analyses were performed by ASTM method D 1915 (1979) except that the individual sugars were determined by HPLC on a Bio-Rad HPX-85 carbohydrate column instead of by paper chromatography. The column temperature was maintained at 85 C. Water was used to elute the column. An RI detector was used to monitor the chromatograms. Determination of sugars by HPLC was shown to be comparable to paper chromatography and to have the same order of precision (Schwandt 1980).

Uronic anhydride was determined by a dehydration procedure (Scott 1979), and by the Browning method (1949).

Acetyl analysis

The acetyl content was determined by an alkaline hydrolysis procedure (Wiesenberger 1947).

Ash analysis

The ash analysis was determined by ASTM method D 1102 (1978).

Lignin analysis

The lignin was determined as the insoluble residue obtained after the primary hydrolysis with 72% sulfuric acid in the sugar analyses. This is equivalent to ASTM method D 1106 (1977).

CONCLUSIONS

Xylan removal from hardwoods by water prehydrolysis (autohydrolysis) can be modeled kinetically as the sum of two parallel first-order reactions—one fast and one slow. The rate constant for initial xylan removal usually reported in the

literature was shown to be a complex function of both the fast and slow rates. The rate constants for the fast and slow reactions are highly correlated. The slower xylan removal reaction may be due to a portion of xylan being embedded within or attached to lignin via lignin-carbohydrate bonds.

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